

Lead recovery from a typical Brazilian sludge of exhausted lead-acid batteries using an electrohydrometallurgical process

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Abstract

Lead recovery from the nonmetallic portion of exhausted lead-acid batteries, also called sludge, was investigated using an electrohydrometallurgical process. Among 13 aqueous solutions studied in solubility tests, only the following three were chosen for the whole process (leaching and electrowinning steps): tetrafluoroboric acid (200 g/L), glycerol (92 g/L) + sodium hydroxide (120 g/L) and sodium potassium tartrate (150 g/L) + sodium hydroxide (150 g/L). The tetrafluoroboric acid showed an attractive performance as leaching electrolyte due to its low cost and reasonable leaching strength. In the electrowinning process using the solution obtained from the leaching of a desulfated sludge with this acidic electrolyte, compact, adherent and highly pure lead deposits were produced at 250 A/m². Scanning electron micrographs (SEM) of lead deposits obtained at different current densities in the range of 250–500 A/m² revealed a marked influence of the current density on the deposit morphology.
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1. Introduction

The annual production of automotive batteries in Brazil is approximately 15 million units, from which ca. 150,000 t of lead can be recovered. With the new Brazilian government regulations (CONAMA, 1999) for collection and recycling of exhausted batteries,

most of the producers of lead-acid batteries established the goal of increasing the use of lead yielded from the recycling of practically 100% of these batteries. Nowadays, lead recovery from exhausted batteries is carried out by the pyrometallurgical route, which may cause environmental problems like the emission into the atmosphere of considerable amounts of dust containing lead particulate and sulfur oxides (Valdez, 1997). An alternative route is the electrohydrometallurgical one, as it might meet the environmental requirements (Maja et al., 1993) and also

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reduce operating costs. Consequently, a number of pilot plants based on this route have been proposed and investigated (Prengaman, 1995; Ginatta, 1984; Maja et al., 1990; Olper, 1988, 1998).

The electrohydrometallurgical route comprises a preliminary stage in which the exhausted lead-acid batteries are crushed, followed by a separation into sulfuric acid and the plastic, metallic and nonmetallic portions. The plastic portion is submitted to reprocessing and the metallic portion is remelted. The non-metallic portion, also called battery sludge, consists of distinct lead compounds, basically metallic lead (Pb), lead dioxide (PbO_2), lead sulfate (PbSO_4) and also lead oxide (PbO); small amounts of glass, synthetic fibers, carbon, rubber, paper, PVC separators and granular silica may also be present. Due to the low solubility of lead sulfate in acidic media, the battery sludge is treated with ammonium (or sodium) carbonate or sodium hydroxide solutions to transform the lead sulfate into lead carbonate or hydroxide (desulfuration process) (Morachevskii, 1997; Chen and Dutrizac, 1996). After desulfating the sludge, the remaining residue is leached using a suitable electrolyte to solubilize the lead compounds; lead is then recovered from solution by electrowinning using insoluble anodes (Ginatta, 1984; Maja et al., 1990;

Olper, 1988). The major problem associated with lead electrowinning in acidic media is that lead is deposited in the dendritic form on the cathode simultaneously with the parasitic formation of PbO_2 on the anode (Maja et al., 1993). In order to avoid the formation of this undesirable oxide, a diaphragm cell was proposed for lead electrowinning (Olper, 1998). In this cell, an acidic electrolyte (HBF_4) containing Pb^{2+} ions and also the redox couple $\text{Fe}^{2+}/\text{Fe}^{3+}$ is separated by a membrane. So, lead deposition occurs in the cathode compartments and Fe^{2+} oxidation in the anode compartments. Alkaline electrolytes have also been proposed for lead electrowinning, giving a stable electrolysis process (Morachevskii et al., 1996; Weiping et al., 1996, 1997). Table 1 shows the main characteristics of the existing/proposed processes for lead recovery from exhausted lead-acid batteries.

Most of the works reported in papers and patents concerning lead recovery from exhausted lead-acid batteries start from a sludge with metallic lead and antimony contents of 13% (Maja et al., 1990). The high content of these metals in the sludge is very important for its leaching because such metals react spontaneously with the lead dioxide also present in the sludge, reducing most of the Pb^{4+} to Pb^{2+} ions. However, this is not the case of typical Brazilian

Table 1
Process for lead recovery

Processes for lead recovery	Advantages	Disadvantages
Thermal conventional	Long history of industrial use	High environmental impact and high temperature and cost
Electrowinning in acidic media— HBF_4 (Ginatta, 1984; Maja et al., 1990; Olper, 1988)	Low environmental impact, current efficiency of 99%, energy consumption of 800 kW h/t of Pb, deposit purity of 99.98% and low cost	PbO_2 formation on the anodes and anodes (graphite) deterioration
Electrowinning in basic media— NaOH —glycerol (Morachevskii et al., 1996)	Low environmental impact, current efficiency of 85–90%, energy consumption of 400–500 kW h/t of Pb, deposit purity of 99.98%, anodes of stainless steel and desulfating not needed	PbO_2 formation on the anodes and cost of chemicals
Electrowinning in basic media— NaOH — $\text{NaKC}_4\text{H}_4\text{O}_6$ (Weiping et al., 1996, 1997)	Low environmental impact, current efficiency $\geq 98\%$, energy consumption of 400–500 kW h/t of Pb, deposit purity of 99.99%, anodes of stainless steel and desulfating not needed	PbO_2 formation on the anodes and cost of chemicals
Electrowinning in acidic media— HBF_4 with $\text{Fe}^{2+}/\text{Fe}^{3+}$ (Olper, 1998)	Low environmental impact, high current efficiency, energy consumption of 500 kW h/t of Pb, deposit purity of 99.99% and desulfating not needed	Diaphragm cell with membranes

sludges, which contain only less than 5% of metallic lead (Plajax Indústria e Comércio de Plásticos Ltda., 1999). Thus, the electrohydrometallurgical processes described in the literature are not totally appropriate for Brazilian companies. Therefore, in the present experimental work, carried out at laboratory scale, the main objective was to develop a suitable and competitive process for lead recovery from a typical sludge obtained by Brazilian companies from exhausted lead-acid batteries. The leaching and the electrowinning processes using aqueous alkaline and acidic electrolytes were investigated. The morphology of the lead deposits obtained at different current densities in one of these media was also examined.

2. Experimental

2.1. Origin and treatment of the sludge

Samples of an industrial sludge provided by Plajax Indústria e Comércio de Plásticos Ltda. (Bauru, SP, Brazil) were investigated. The PbO, PbO₂, PbSO₄ and Pb contents in the sludge were determined by EDTA titration. Mineralogical characterization was carried out using a Siemens D5000 X-ray diffractometer.

The sludge was firstly treated with NaOH in order to convert all PbSO₄ to Pb(OH)₂. For this desulfuration process, a mixture of sludge, sodium hydroxide and water in the mass ratio of 100:18:75 was vigorously stirred during 1 h using a magnetic stirrer.

2.2. Solubility tests

Samples (~ 1 g) of the original sludge, as well as pure PbO, PbO₂, PbSO₄ and analytical grade Pb were submitted to qualitative solubility tests in 10 mL of the following aqueous electrolytes kept at room temperature: concentrated sulfuric acid; tetrafluoroboric acid (200 g/L); methanesulfonic acid (400 g/L); saturated oxalic acid (9.8 g/L); citric acid (384 g/L); glycerol (184 g/L); sodium hydroxide (120 g/L); glycerol (92 g/L)+sodium hydroxide (120 g/L); ascorbic acid (10 g/L); glycerol (92 g/L)+sodium hydroxide (120 g/L)+ascorbic acid (10 g/L); glycerol (92 g/L)+ascorbic acid (10 g/L); acetic acid (360 g/L) and sodium potassium tartrate (150 g/L)+sodium hydroxide (150 g/L).

2.3. Leaching tests

After the solubility tests, only the electrolytes tetrafluoroboric acid (200 g/L), glycerol (92 g/L)+sodium hydroxide (120 g/L) and sodium potassium tartrate (150 g/L)+sodium hydroxide (150 g/L) were selected for the leaching tests. Thus, mixtures of the original or desulfated sludge with the mentioned electrolytes were prepared in the concentration of 200 g/L and then stirred for different times. The Pb²⁺ concentration in the resultant aqueous electrolytes was determined complexometrically, using eriochrome black T as indicator. An aqueous solution of 0.01 M Na₂EDTA was added until the indicator color changed from violet to blue (Vogel and Svehla, 1996). In strongly alkaline media, a white precipitate of Pb(OH)₂ was observed in the aliquots previously diluted with water; this precipitate was immediately dissolved by adding some drops of the Na₂EDTA solution with subsequent titration.

2.4. Electrowinning tests

Firstly, only electrowinning tests using aqueous electrolytes obtained by dissolving analytical grade PbO in the electrolytes tetrafluoroboric acid (200 g/L), glycerol (92 g/L)+sodium hydroxide (120 g/L) and sodium potassium tartrate (100 g/L)+sodium hydroxide (100 g/L) were investigated. These tests were carried out under magnetic stirring in a glass cell of about 600 mL containing three electrodes: a strip from an AISI-304 stainless-steel foil (Acesita) as cathode (15 cm²) and two graphite bars as anodes (80 cm²), for the acidic electrolyte; three strips from the same stainless-steel foil, one being the cathode (10 cm²) and two the anodes (20 cm²), for the alkaline electrolytes. Phosphoric (1 g/L) and boric (10 g/L) acids were used as additives only in the acidic electrolyte. While the first acid was added to inhibit the formation of PbO₂ on the anode, the second was added to tie up the free HF or F⁻ ions in the electrolyte (Tam, 1986). In order to improve the quality of the lead deposits, animal gelatin (2 g/L) was also used as additive in both acidic and alkaline electrolytes. Different current densities (200, 250, 300, 350, 400, 450 and 500 A/m²) were used during a time sufficient to consume approximately 60% of the initial Pb²⁺ concentration in the aqueous electrolyte (200 mL of acidic or alkaline

electrolyte containing 100 g/L of Pb^{2+} ions). Current was applied using a Dower PS-3003D DC power supply and monitored with a Dower DM-1010 multimeter. The cell voltage was monitored with a Minipa ET-20002 multimeter.

After electrowinning tests using aqueous electrolytes obtained by dissolving analytical grade PbO in the electrolytes tetrafluoroboric acid (200 g/L), glycerol (92 g/L) + sodium hydroxide (120 g/L) and sodium potassium tartrate (100 g/L) + sodium hydroxide (100 g/L), only the first was chosen for the leaching tests using samples of desulfated sludge. The lead recovery from the resultant acidic electrolyte was carried out using the same experimental conditions described above.

The quality of the lead deposits obtained from the acidic electrolyte at different current densities in the range 250–500 A/m² was evaluated by scanning electron microscopy (SEM) using a Leica Cambridge equipment (model Stereoscan 440).

3. Results and discussion

According to a Brazilian company (Plajax Indústria e Comércio de Plásticos Ltda., 1999), the components of the lead-acid batteries after crushing and washing operations are: grids (~ 28%), polypropylene (~ 8%), sludge (~ 48%) and other residues such as PVC separators, rubbers, ebonite, fibers, organic additives, etc. (~ 16%). The battery grids contain more than 90% of metallic lead and are readily remelted. The original sludge, however, is more complex and is known to contain PbSO_4 in addition to a number of other lead compounds. X-ray diffraction analysis of an original sludge (Fig. 1a) showed the presence of PbSO_4 , PbO (litharge), $\text{PbO} \cdot \text{PbSO}_4$, $\alpha\text{-PbO}_2$ and metallic Pb, in agreement with the literature (Maja et al., 1990). On the other hand, an X-ray diffractogram of a desulfated sludge (Fig. 1b) exhibited only the presence of lead hydroxides [$\text{Pb}(\text{OH})_2$, $2\text{PbO} \cdot \text{Pb}(\text{OH})_2$ and $3\text{PbO} \cdot 2\text{Pb}(\text{OH})_2$]; the peaks associated with PbSO_4 and $\text{PbO} \cdot \text{PbSO}_4$ were not observed.

After washing a sample of the original sludge, a solution of pH 6 was obtained, indicating the absence of sulfuric acid. The lead compounds content in the original and desulfated sludge, determined by differ-

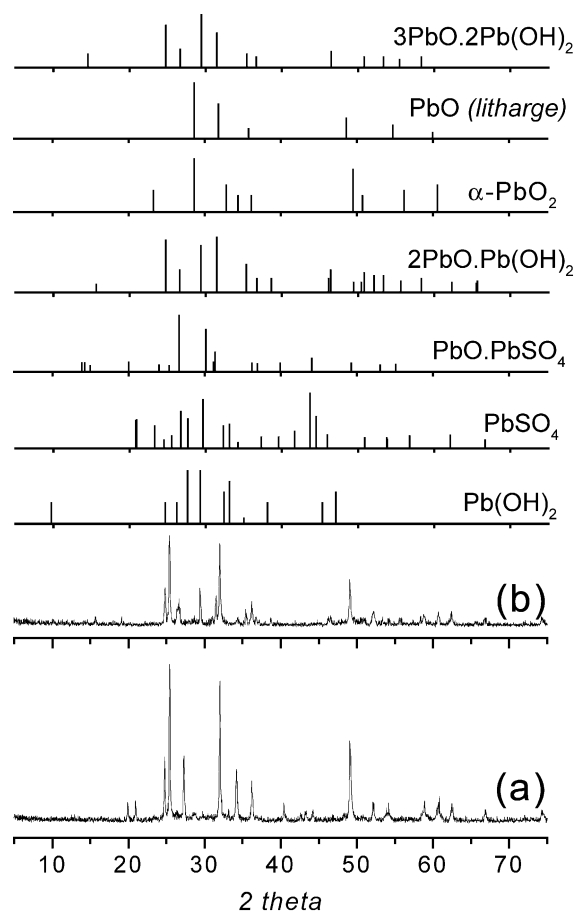


Fig. 1. X-ray powder diffractograms of some standard lead compounds and of Brazilian sludges from exhausted lead-acid batteries (a) original and (b) desulfated.

ent experimental procedures including each one an EDTA titration, are summarized in Table 2. After solubilizing the lead compounds in both original and desulfated sludges, a heterogeneous and pulverized residue was found; it consists probably of polypropylene, silica, PVC, etc. As shown in Table 2, the original sludge comprises major amounts of PbSO_4 and PbO_2 together with minor amounts of PbO and metallic Pb. Therefore, pure Pb can be recovered from ca. 70% of the original sludge. The PbSO_4 content in the desulfated sludge was negligible, denoting the efficiency of the desulfating process used. The high PbO_2 content in both original and desulfated sludge represents the major problem for the leaching process. While PbO and $\text{Pb}(\text{OH})_2$ are readily dissolved by

Table 2

Chemical composition of a typical Brazilian sludge from exhausted lead-acid batteries

Compound	Sludge composition (%) (m/m)	
	Original	Desulfated
PbSO ₄	50	<0.1
Pb(OH) ₂	–	52
PbO ₂	28	35
PbO	9	–
Pb	4	8

most of the leaching electrolytes, PbO₂ requires the reduction of Pb⁴⁺ to Pb²⁺ prior to the leaching process.

The observations of the qualitative solubility tests carried out at room temperature using samples of original sludge in different aqueous electrolytes are summarized in Table 3. The following decreasing order of solubilizing strength was found: tetrafluoroboric acid (200 g/L) $\cong$ glycerol (92 g/L) + sodium hydroxide (120 g/L) $\cong$ glycerol (92 g/L) + sodium hydroxide (120 g/L) + ascorbic acid (10 g/L) $\cong$ glycerol (92 g/L) + ascorbic acid (10 g/L) > ascorbic acid (10 g/L) $\cong$ acetic acid (360 g/L) $\cong$ sodium potassium tartrate (150 g/L) + sodium hydroxide (150 g/L) $\cong$ sodium hydroxide (120 g/L) $\gg$ concentrated sulfuric acid $\cong$ methanesulfonic acid (400 g/L) $\cong$ citric acid (384 g/L). Samples of the original sludge were completely solubilized in the ascorbic acid solution, but the formation of an undesirable solid residue was observed after 24 h. Samples of original sludge and PbO were not solubilized by the saturated oxalic acid and the glycerol solutions. For most of the aqueous electrolytes tested, a solid residue, most probably PbO₂, was observed at the end of the solubility tests. This is probably due to the low content of metallic lead in the original sludge, hindering the reduction of Pb⁴⁺ to Pb²⁺ ions in the qualitative solubility studies.

From the previous results, the following aqueous electrolytes were selected for the quantitative leaching tests of samples of original and desulfated sludge: tetrafluoroboric acid (200 g/L), glycerol (92 g/L) + sodium hydroxide (120 g/L), and sodium potassium tartrate (150 g/L) + sodium hydroxide (150 g/L). The leaching strength was evaluated by determining the Pb²⁺ ions concentration after the leaching tests (see Fig. 2). For the original sludge, sodium potassium

tartrate (150 g/L) + sodium hydroxide (150 g/L) presented the best leaching strength followed by tetrafluoroboric acid (200 g/L). However, a large amount of solid residue was observed when tetrafluoroboric acid (200 g/L) was used, due to the presence of insoluble lead sulfate in the original sludge. When glycerol (92 g/L) + sodium hydroxide (120 g/L) was tested, the amount of a white residue increased as the leaching time was increased. The continuous Pb(OH)₂ precipitation may probably explain the formation of such residue; similar results have been reported in the literature (Morachevskii et al., 1996). For the desulfated sludge tetrafluoroboric acid (200 g/L) and sodium potassium tartrate (150 g/L) + sodium hydroxide (150 g/L) presented similar leaching strengths.

Table 3

Observations of the solubility tests for the original sludge and lead compounds at room temperature

Electrolyte	Time	Sludge	Pb	PbO	PbO ₂	PbSO ₄
Concentrated sulfuric acid	1h	i	i	s	i	i
	1d	p	i	s	i	i
Tetrafluoroboric acid (200 g/L)	1h	p	i	s	i	i
	1d	p	i	s	i	i
Methanesulfonic acid (400 g/L)	1h	i	i	s	i	i
	1d	i	i	s	i	i
Saturated oxalic acid (9.8 g/L)	1h	i	i	i	i	i
	1d	i	i	i	i	i
Citric acid (384 g/L)	1h	i	i	s	i	i
	1d	i	i	s	s	i
Glycerol (184 g/L)	1h	i	i	i	i	i
	1d	i	i	i	i	i
Sodium hydroxide (120 g/L)	1h	i	i	i	i	s
	1d	i	i	i	i	s
Glycerol (92 g/L) + sodium hydroxide (120 g/L)	1h	p	i	s	i	s
	1d	s	i	s	p	s
Ascorbic acid (10 g/L)	1h	p	i	s	s	i
	1d	p	i	s	s	i
Glycerol (92 g/L) + ascorbic acid (10 g/L) + sodium hydroxide (120 g/L)	1h	s	i	s	s	s
	1d	s	i	s	s	s
Glycerol (92 g/L) + ascorbic acid (10 g/L)	1h	p	i	s	s	i
	1d	p	i	s	s	i
Acetic acid (360 g/L)	1h	i	i	s	i	s
	1d	p	i	s	i	s
Sodium potassium tartrate (150 g/L) + sodium hydroxide (150 g/L)	1h	i	i	s	i	s
	1d	p	i	s	i	s

h: hour; d: day; s: soluble; p: partially soluble and i: insoluble.

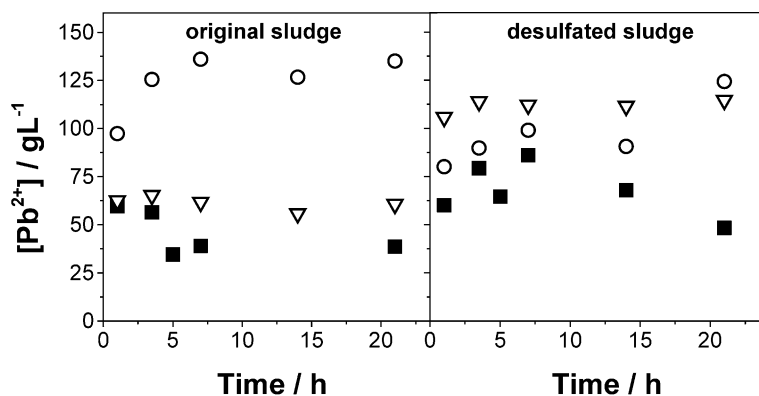


Fig. 2. Pb^{2+} concentration for the leaching tests of the original and desulfated sludge using (O) sodium potassium tartrate (150 g/L)+sodium hydroxide (150 g/L); (■) glycerol (92 g/L)+sodium hydroxide (120 g/L) and (▽) tetrafluoroboric acid (200 g/L).

As mentioned before, the electrowinning tests were firstly carried out using electrolytes obtained by dissolving analytical grade PbO in the electrolytes tetrafluoroboric acid (200 g/L), glycerol (92 g/L)+sodium hydroxide (120 g/L), and sodium potassium tartrate (100 g/L)+sodium hydroxide (100 g/L). The results obtained in these tests are summarized in Table 4. Cathodic current efficiency (CCE), specific energy consumption (SEC) and the quality of the lead deposits were estimated and compared among the different electrolytes investigated. Although the lead deposits were compact for the three electrolytes, high values of cathodic current efficiency (99%) were obtained only

for tartrate and tetrafluoroboric acid. Despite the lower specific energy consumption obtained for the tartrate electrolyte, only the tetrafluoroboric electrolyte was chosen for the electrowinning tests at different current densities due to its low cost. The results obtained in several of these experiments are presented in Table 5. As the current density increased, the specific energy consumption increased while the cathodic current efficiency was practically constant. On the other hand, the quality of the lead deposits was strongly affected by the current density; good lead deposits were obtained only for current density values lower than 400 A/m^2 . Coincidentally, the graphite anodes were less deteriorated for this same range of current densities. Compact, uniform and adherent lead deposits were obtained in all cases, except for the lead deposit

Table 4

Cell potential (E), cathodic current efficiency (CCE), specific energy consumption (SEC), and quality of lead deposits obtained in electrowinning tests using different electrolytes

Electrolyte	E (V)	CCE (%)	SEC (W h/kg)	Deposit quality
Tartrate ^a	1.48–1.55	99 ^b	390	C ^c
Glycerol ^d	1.43–1.70	90 ^b	430	C
Acidic ^e	2.25–2.30	99 ^f	590	C

^a Sodium potassium tartrate (150 g/L)+sodium hydroxide (150 g/L)+animal gelatin (2 g/L).

^b $i = 200 \text{ A/m}^2$.

^c C compact deposit.

^d Glycerol (92 g/L)+sodium hydroxide (120 g/L)+animal gelatin (2 g/L).

^e Tetrafluoroboric acid (200 g/L)+phosphoric (1 g/L) and boric (10 g/L) acids+animal gelatin (2 g/L).

^f $i = 250 \text{ A/m}^2$.

Table 5

Cell potential (E), cathodic current efficiency (CCE), specific energy consumption (SEC), and quality of lead deposits obtained in electrowinning tests at different current densities using the acidic electrolyte

i (A/m ²)	E (V)	CCE (%)	SEC (W h/kg)	Deposit quality
250	2.25–2.30	99	590	C
300	2.30–2.50	99	610	C
350	2.30–2.40	99	600	C
400	2.30–2.45	99	625	C+D
450	2.30–2.45	99	622	C+D
500	2.50–2.70	99	650	D

C—compact deposit; D—dendritic deposit; C+D—compact in the center and dendritic in the corners of the deposit.

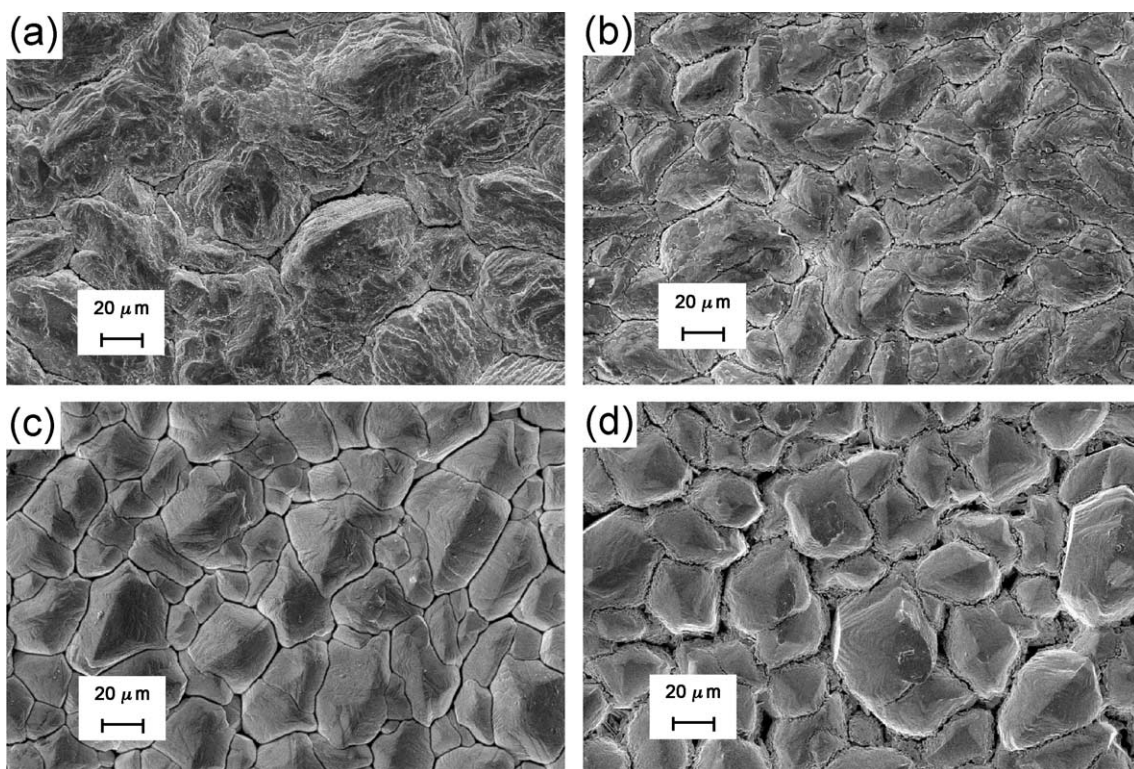


Fig. 3. Scanning electron micrographs of various lead deposits recovered at different current densities from analytical grade PbO in a tetrafluoroboric acid (200 g/L) solution, containing phosphoric (1 g/L) and boric (10 g/L) acids and animal gelatin (2 g/L). (a) 250 A/m²; (b) 300 A/m²; (c) 400 A/m² and (d) 450 A/m².

obtained at 500 A/m², where dendritic, rugous and voluminous deposit was observed.

Fig. 3 presents scanning electron micrographs (SEM) of various lead deposits obtained at different current densities from an electrolyte prepared by dissolving analytical grade PbO in a tetrafluoroboric acid (200 g/L) solution containing phosphoric (1 g/L) and boric (10 g/L) acids and animal gelatin (2 g/L) as additives. The lead deposits obtained in the current density range 250–400 A/m² (Fig. 3a, b and c) present similar morphologies, i.e. compact, uniform and adherent lead deposits. Only the lead deposit obtained at 450 A/m² (Fig. 3d) presents pyramid-like small particles around the grains.

Taking into account all the above results and also the lower cost of tetrafluoroboric acid, the lead recovery from samples of desulfated sludge of exhausted lead-acid batteries was carried out using only this acidic electrolyte [tetrafluoroboric acid (200 g/

L)], containing phosphoric (1 g/L) and boric (10 g/L) acids and animal gelatin (2 g/L) as additives. For these experiments, the leaching time used was always 1 h. The electrowinning tests were always performed at a constant current density of 250 A/m². In this case, compact, uniform and adherent lead deposits were also obtained. Moreover, highly pure lead was produced. A micrograph of a typical lead deposit obtained in these experimental conditions is illustrated in Fig. 4. The morphology of this lead deposit is a little different from those shown in Fig. 3, probably due to the presence of another organic additive in the solution (lignin), as this substance is usually added to the electrolyte of lead-acid batteries in order to extend their useful life (Plajax Indústria e Comércio de Plásticos Ltda., 1999). In order to thicken the lead deposit, several subsequent electrowinning tests were also carried out during a time sufficient to consume, for each test, approximately 60% of the initial Pb²⁺

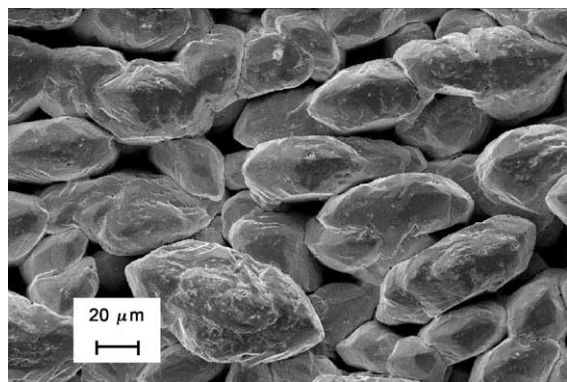


Fig. 4. Scanning electron micrograph of a typical lead deposit recovered at 250 A/m^2 from an electrolyte obtained by leaching desulfated sludge from exhausted lead-acid batteries in a tetrafluoroboric acid (200 g/L) solution, containing phosphoric (1 g/L) and boric (10 g/L) acids and animal gelatin (2 g/L).

concentration in the aqueous electrolyte. After nearly 120 h, a 2–3-mm-thick, compact, uniform and adherent lead deposit was obtained. The PbO_2 weight formed at the anodes was less than 1% of the lead electrowon at the anode.

4. Conclusions

Unlike the battery sludge obtained from exhausted lead-acid batteries in other countries, the Brazilian sludge contains a low content of metallic lead. Due to this fact, none of the leaching electrolytes investigated in this work totally dissolved such sludge. Lead dioxide was the majority component in the solid residue after the leaching tests.

Tetrafluoroboric acid showed an attractive performance as leaching electrolyte, due to its reasonable leaching strength and low cost. When the desulfated sludge obtained from exhausted lead-acid batteries was leached with this acidic electrolyte, compact, adherent and highly pure lead deposits were electrowon. Therefore, the electrohydrometallurgical process used in this work presented a suitable and promising performance for lead recovery from a typical Brazilian sludge of exhausted lead-acid batteries.

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